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(54) Title: **METHOD FOR COLOURING HAIR**

(57) Abstract: A method of providing a colour change to human or animal hair wherein the method comprises the steps of (a) applying to hair a hair colour altering composition, (b) leaving the hair colour altering composition on the hair for from about 0.5 to about 15 minutes and then (c) optionally, rinsing the hair colour altering composition from the hair, wherein steps (a) and (b) and (c) are repeated from about once a month to about 3 times a day. A multiple application method of the invention provides an increase in colour change (as measured by Delta E) compared with conventional methods which use a single application of hair colouring composition for around 20-30 minutes. In addition, the method of the present invention is no more damaging to the hair compared with conventional single application methods.

Method for Colouring Hair

Technical Field

This invention relates to methods for altering the colour of human or animal hair, and more especially to methods which are convenient and which provide excellent hair colouring and conditioning.

Background of the Invention

The desire to alter the color of human hair is not a facet of modern times. Since the days of the Roman Empire the color of human hair has been routinely altered to accommodate the changes of fashion and style. However the attainment of precise initial colors which are retained by the hair for a desirable period has remained a more elusive goal. The difficulties in the development of hair coloring compositions which can deliver precise long-lasting colors are in part due to the inherent structure of the hair itself and in part due to the necessary conditions of effective hair coloration processes. Common difficulties with conventional hair coloring compositions include color fade, wash fade, irregular dye uptake, hair damage and brittleness, skin irritation, odor and skin staining.

Over the years significant effort has been directed towards the elimination of many of the problems associated with the dyeing of human hair. Various approaches to hair dyeing have been developed, these include, direct action dyes, natural dyes, metallic dyes and oxidative dyes.

Oxidative dyes are commonly used to provide permanent colour to the hair. A conventional method for colouring hair using oxidative dyes involves applying to dry hair a hair colouring composition containing oxidative dyes and an oxidising agent and leaving the composition on the hair for around 20-30 minutes before the composition is rinsed from the hair.

Although this method of colouring hair has been used for many years as a way of providing a wide range of permanent shades to the hair, this method suffers from several disadvantages.

Firstly, conventional methods require an oxidative dye composition to be left on the hair for a relatively long period of time, on average around 30 minutes, in order to allow enough time for a colour to develop on the hair. Therefore if the consumer wishes to colour their hair using a conventional method, they have to find time to do this outside of the relatively short period of time they spend on the normal hair treatment regime, namely, shampooing and conditioning. In addition, methods using oxidative dye technology can cause damage to the hair. Damaging effects can include dryness, brittleness and breakage. Also, many such compositions and methods are inconvenient to use. For example, in the case of conventional hair colouring compositions and methods using oxidative dye technology the hair is treated with a mixture of oxidative hair colouring agents and an oxidising agent. Hydrogen peroxide is the most commonly used oxidising agent. Usually, the product is sold as a kit containing separately packaged hair dye components and oxidising components. The consumer is then instructed to mix the two components together prior to application on the head. This is time consuming and messy for the consumer.

It has now surprisingly been found that the hair colouring method of the present invention which comprises short multiple applications of hair colour altering composition to the hair provides a greater colour change (as measured by Delta E) than conventional methods wherein a single application of dye composition is used and left on the hair for around 20-30 minutes. In addition, it has surprisingly been found that the method of the present invention provides greater colour changes (as measured by Delta E) without increasing damage to the hair. Furthermore, the method of the present invention provides improved conditioning, in particular improved ease of combing. In addition the method of the present invention provides increased convenience and ease of use. Indeed, it is an object of the present invention to provide a method of hair colouring which can be used as part of the conventional cleansing and conditioning routine used by consumers in the bath and shower.

All percentages are by weight of the final compositions in the form intended to be used unless specified otherwise.

Summary of the Invention

The subject of the present invention is a method of altering the colour of human or animal hair.

According to one aspect of the present invention, there is provided a method of providing permanent, semi-permanent or demi-permanent colour to human or animal hair wherein the method comprises the steps of (a) applying to hair a hair colour altering composition, (b) leaving the hair colour altering composition on the hair for from about 0.5 to about 15 minutes and then (c) optionally, rinsing the hair colour altering composition from the hair, wherein steps (a), (b) and (c) are repeated from about once a month to about 3 times a day.

It is to be understood that the percentage weights of the composition components herein are expressed in terms of the total composition, and refers to the composition in the form of intended use, i.e. the final composition which is intended for application to the hair.

Detailed Description of the Invention

The hair colouring method according to the present invention comprises the steps of (a) applying to hair a hair colour altering composition, (b) leaving the hair colour altering composition on the hair for about 0.5 to about 15 minutes and then (c) optionally, rinsing the hair colour altering composition from the hair, wherein steps (a), (b) and (c) are repeated from about once a month and to about 3 times a day, preferably from about once a week to about 7 times a week, preferably from about 2 times to about 6 times a week, more preferably from about 2 times to about 4 times a week.

In order to get the desired colour change (as measured by Delta E) it is preferable that steps (a), (b) and (c) are repeated at least 4 times in total, preferably at least 6 times in total.

In preferred methods of the invention, the hair colour altering composition is rinsed from the hair after step (b).

In preferred methods of the invention, the method also comprises a step (a1) of shampooing the hair and rinsing the shampoo from the hair immediately before step (a). In this case it is preferred therefore that steps (a1), (a), (b) and (c) are repeated from about once a month to about 3 times a day, preferably from about once a week and about 7 times a week, preferably between about 2 times a week and about 6 times a week, more preferably between about 2 times and about 4 times a week. It is also preferable that the hair colour altering composition is applied to wet hair, which has been shampooed or otherwise.

It is preferable that the hair colour altering composition is left on the hair for from about 0.5 minutes to about 5 minutes, preferably from about 1 minute to about 5 minutes, more preferably from about 1 minute to about 3 minutes. Since this method relies on using short multiple applications of a hair colouring composition compared to conventional methods which use a "one-shot" 20-30 minute application of a hair colouring composition, the present method is ideal for use in the shower, particularly as part of the conventional shampoo and conditioning regime.

The methods of the present invention are used to deliver permanent, semi-permanent or demi-permanent colour changes to the hair, preferably permanent, such as for example by using oxidative hair colouring agents.

As used herein the term 'hair' to be treated may be 'living' i.e. on a living body or may be 'non-living' i.e. in a wig, hairpiece or other aggregation of non-living fibres, such as those used in textiles and fabrics. Mammalian, preferably human hair is preferred. However wool, fur and other melanin containing fibres are suitable substrates for the compositions according to the present invention.

As used herein the term 'hair colour altering composition' is used in the broad sense in that it is intended to encompass compositions containing at least one hair colour altering agent. Thus, the term 'hair colour altering composition' is intended to apply to compositions which contain, in addition to at least one hair colour altering agent, such things as, by way of example, but not limited to oxidising agents, oxidising aids, sequestrants, stabilisers, thickeners, buffers, carriers, surfactants, solvents, antioxidants, polymers, UV filters and additional conditioning agents.

Hair Colour Altering Composition

The hair colour altering compositions herein comprise at least one hair colour altering agent.

Hair Colour Altering Agents

The hair colour altering agent herein can be any colouring agent suitable for use in altering the colour of the hair. Suitable hair colour altering agents include, but are not limited to, oxidative

dyes, photographic dyes, acid dyes, neutral dyes, cationic dyes, reactive dyes, VAT dyes, and mixtures thereof. Bleaching agents such as hydrogen peroxide can also be classed as a hair colour altering agent herein since although it is not a colouring agent, it alters the colour of the hair (as measured by Delta E), i.e. bleaching. Particularly preferred for use herein are oxidative dyes.

The hair color altering compositions used in the method of the present invention preferably include an oxidative or non-oxidative hair coloring agent. Such hair coloring agents are used to formulate permanent, demi-permanent, semi-permanent hair dye compositions.

Permanent hair dye compositions as defined herein are compositions which once applied to the hair are substantially resistant to wash-out. Demi-permanent hair dye compositions as defined herein are compositions which are substantially removed from the hair after up to 24 washes. Semi-permanent hair dye compositions as defined herein are compositions which once applied to the hair are substantially removed from the hair after up to 10 washes. Temporary hair dye compositions as defined herein are compositions which once applied to the hair are substantially removed from the hair after up to 2 washes. These different types of hair coloring compositions can be formulated via the specific combination of oxidant and/or dyes at different levels and ratios. Wash out as defined herein is the process by which hair color is removed from the hair over time during normal hair cleansing regimen. Washfastness as defined herein, means, the resistance of the dyed hair to wash out.

Oxidative hair coloring agents

A preferred hair coloring agent herein is an oxidative hair coloring agent. The concentration of each oxidative hair coloring agent in the coloring compositions according to the present invention is preferably from about 0.001% to about 3% by weight, more preferably from about 0.01% to about 2% by weight.

The total combined level of oxidative hair coloring agents in the compositions used in the methods of the present invention is from about 0.001% to about 5%, preferably from about 0.01% to about 4%, more preferably from about 0.1% to about 3%, most preferably from about 0.1% to about 1% by weight.

Any oxidative hair coloring agent can be used in the compositions herein. Typically, but without intending to be limited thereby, oxidative hair coloring agents, consist essentially of at least two components, which are collectively referred to as dye forming intermediates (or precursors). Dye forming intermediates can react in the presence of a suitable oxidant to form a colored molecule.

The dye forming intermediates used in oxidative hair colorants include: aromatic diamines, aminophenols, various heterocycles, phenols, naphthols and their various derivatives. These dye forming intermediates can be broadly classified as; primary intermediates and secondary intermediates. Primary intermediates, which are also known as oxidative dye precursors, are chemical compounds which become activated upon oxidation and can then react with each other and/or with couplers to form colored dye complexes. The secondary intermediates, also known as color modifiers or couplers, are generally colorless molecules which can form colors in the presence of activated precursors/primary intermediates, and are used with other intermediates to generate specific color effects or to stabilise the color.

Primary intermediates suitable for use in the compositions and processes herein include: aromatic diamines, polyhydric phenols, amino phenols and derivatives of these aromatic compounds (e.g., N-substituted derivatives of the amines, and ethers of the phenols). Such primary intermediates are generally colorless molecules prior to oxidation.

While not wishing to be bound by any particular theory it is proposed herein that the process by which color is generated from these primary intermediates and secondary coupler compounds generally includes a stepwise sequence whereby the primary intermediate can become activated (by oxidation), and then enjoin with a coupler to give a dimeric, conjugated colored species, which in turn can enjoin with another 'activated' primary intermediate to produce a trimeric conjugated colored molecule.

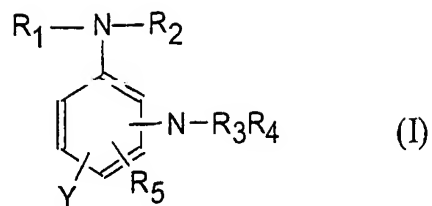
Oxidative Dye Precursors

In general terms, oxidative dye primary intermediates include those monomeric materials which, on oxidation, form oligomers or polymers having extended conjugated systems of electrons in their molecular structure. Because of the new electronic structure, the resultant oligomers and polymers exhibit a shift in their electronic spectra to the visible range and appear colored. For

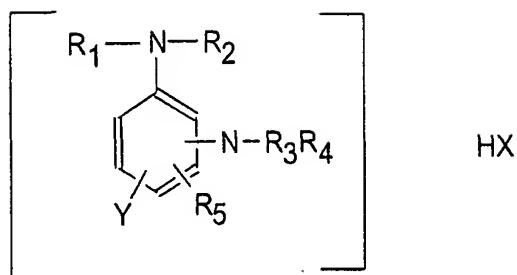
example, oxidative primary intermediates capable of forming colored polymers include materials such as aniline, which has a single functional group and which, on oxidation, forms a series of conjugated imines and quinoid dimers, trimers, etc. ranging in color from green to black. Compounds such as p-phenylenediamine, which has two functional groups, are capable of oxidative polymerization to yield higher molecular weight colored materials having extended conjugated electron systems. Oxidative dyes known in the art can be used in the compositions according to the present invention. A representative list of primary intermediates and secondary couplers suitable for use herein is found in Sagarin, "Cosmetic Science and Technology", Interscience, Special Ed. Vol. 2 pages 308 to 310. It is to be understood that the primary intermediates detailed below are only by way of example and are not intended to limit the compositions and processes herein.

The typical aromatic diamines, polyhydric phenols, amino phenols, and derivatives thereof, described above as primary intermediates can also have additional substituents on the aromatic ring, e.g. halogen, aldehyde, carboxylic acid, nitro, sulfonic acid and substituted and unsubstituted hydrocarbon groups, as well as additional substituents on the amino nitrogen and on the phenolic oxygen, e.g. substituted and unsubstituted alkyl and aryl groups.

Examples of suitable aromatic diamines, amino phenols, polyhydric phenols and derivatives thereof, respectively, are compounds having the general formulas (I), (II) and (III) below:



OR



wherein Y is hydrogen, halogen, (e.g. fluorine, chlorine, bromine or iodine), nitro, amino, hydroxyl,



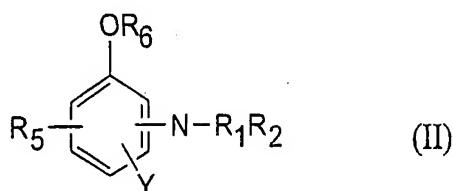
-COOM or -SO₃M (where M is hydrogen or an alkali or alkaline earth metal, ammonium, or substituted ammonium wherein one or more hydrogens on the ammonium ion is replaced with a 1 to 3 carbon atom alkyl or hydroxyalkyl radical), wherein R₁, R₂, R₃ and R₄ are the same or different from each other and are selected from the group consisting of hydrogen, C₁ to C₄

alkyl or alkenyl and C₆ to C₉ aryl, alkaryl or aralkyl, and R₅ is hydrogen, C₁ to C₄ unsubstituted or substituted alkyl or alkenyl wherein the substituents are selected from those designated as Y, above, or C₆ to C₉ unsubstituted or substituted aryl, alkaryl or aralkyl wherein the substituents are selected from those defined as Y, above. Since the precursors of formula (I) are amines, they can be used herein in the form of peroxide-compatible salts, as noted, wherein X represents peroxide-compatible anions of the type herein before detailed. The general formula of the salt indicated is to be understood to encompass those salts having mono-, di-, and tri-negative anions.

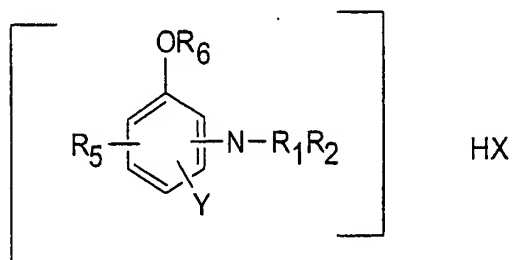
Specific examples of formula (I) compounds are: o-phenylenediamine, m-phenylenediamine, p-phenylenediamine, 2-chloro-p-phenylenediamine, 2-iodo-p-phenylenediamine, 4-nitro-o-phenylenediamine, 2-nitro-p-phenylenediamine, 1,3,5-triaminobenzene, 2-hydroxy-p-phenylenediamine, 2,4-diaminobenzoic acid, sodium 2,4-diaminobenzoate, calcium di-2,4-diaminobenzoate, ammonium 2,4-diaminobenzoate, trimethylammonium 2,4-diaminobenzoate, tri-(2-hydroxyethyl)ammonium 2,4-diaminobenzoate, 2,4-diaminobenzaldehyde carbonate, 2,4-diaminobenzenesulfonic acid, potassium 2,4-diaminobenzenesulfonate, N,N-diisopropyl-p-phenylenediamine bicarbonate, N,N-dimethyl-p-phenylenediamine, N-ethyl-N'-(2-propenyl)-p-phenylenediamine, N-phenyl-p-phenylenediamine, N-phenyl-N-benzyl-p-phenylenediamine, N-ethyl-N'-(3-ethylphenyl)-p-phenylenediamine, 2,4-toluenediamine, 2-ethyl-p-phenylenediamine, 2-(2-bromoethyl)-p-phenylenediamine, 2-phenyl-p-phenylenediamine laurate, 4-(2,5-diaminophenyl)benzaldehyde, 2-benzyl-p-phenylenediamine acetate, 2-(4-nitrobenzyl)-p-phenylenediamine, 2-(4-methylphenyl)-p-phenylenediamine, 2-(2,5-diaminophenyl)-5-methylbenzoic acid, methoxyparaphenylenediamine, dimethyl-p-phenylenediamine, 2,5-dimethylpara-phenylenediamine, 2-methyl-5-methoxy-para-phenylenediamine, 2,6-methyl-5-methoxy-para-phenylenediamine, 3-methyl-4-amino-N,N-diethylaniline, N,N-bis(β -hydroxyethyl)-para-phenylenediamine, 3-methyl-4-amino-N,N-bis(β -hydroxyethyl)aniline, 3-chloro-4-amino-N,N-bis(β -hydroxyethyl)aniline, 4-amino-N-ethyl-N-(carbamethyl)aniline, 3-methyl-4-amino-N-ethyl-N-(carbamethyl)aniline, 4-amino-N-ethyl-(β -piperidonoethyl)aniline, 3-methyl-4-amino-N-ethyl-(β -piperidonoethyl)aniline, 4-amino-N-ethyl-N-(β -morpholinoethyl)aniline, 3-methyl-4-amino-N-ethyl-N-(β -morpholinoethyl)aniline, 4-amino-N-ethyl-N-(β -acetylaminoethyl)aniline, 4-amino-N-(β -methoxyethyl)aniline, 3-methyl-4-amino-N-ethyl-N-(β -acetylaminoethyl)aniline, 4-amino-N-ethyl-N-(β -mesylaminoethyl)aniline, 3-methyl-4-amino-N-ethyl-N-(β -mesylaminoethyl)aniline, 4-amino-N-ethyl-N-(β -sulphoethyl)aniline, 3-methyl-4-amino-N-ethyl-N-(β -

sulphoethyl) aniline, N-(4-aminophenyl)morpholine, N-(4-aminophenyl)piperidine, 2,3-dimethyl p-phenylenediamine, isopropyl-p-phenylenediamine, N,N-bis-(2-hydroxyethyl)-p-phenylenediamine sulphate.

Compounds having the general structure (II) are as follows:



OR

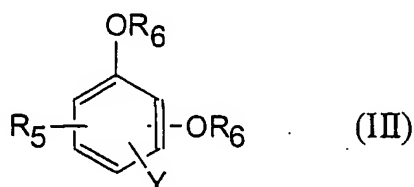


where X and Y are the same as in formula (I), R_1 and R_2 can be the same or different from each other and are the same as in formula (I), R_5 is the same as in formula (I) and R_6 is hydrogen or C_1 to C_4 substituted or unsubstituted alkyl or alkenyl wherein the substituents are selected from those defined as Y in formula (I).

Specific examples of formula (II) compounds are:

o-aminophenol, m-aminophenol, p-aminophenol, 2-iodo-p-aminophenol, 2-nitro-p-aminophenol, 3,4-dihydroxyaniline, 3,4-diaminophenol, chloroacetate, 2-hydroxy-4-aminobenzoic acid, 2-hydroxy-4-aminobenzaldehyde, 3-amino-4-hydroxybenzenesulfonic acid, N,N-diisopropyl-p-aminophenol, N-methyl-N-(1-propenyl)-p-aminophenol, N-phenyl-N-benzyl-p-aminophenol sulphate, N-methyl-N-(3-ethylphenyl)-p-aminophenol, 2-nitro-5-

ethyl-p-aminophenol, 2-nitro-5-(2-bromoethyl)-p-aminophenol, (2-hydroxy-5-aminophenyl)acetaldehyde, 2-methyl-p-aminophenol, (2-hydroxy-5-aminophenyl)acetic acid, 3-(2-hydroxy-5-aminophenyl)-1-propene, 3-(2-hydroxy-5-aminophenyl)-2-chloro-1-propene, 2-phenyl-p-aminophenol palmitate, 2-(4-nitrophenyl)-p-aminophenol, 2-benzyl-p-aminophenol, 2-(4-chlorobenzyl)-p-aminophenol perchlorate, 2-(4-methylphenyl)-p-aminophenol, 2-(2-amino-4-methylphenyl)-p-aminophenol, p-methoxyaniline, 2-bromoethyl-4-aminophenyl ether phosphate, 2-nitroethyl-4-aminophenyl ether bromide, 2-aminoethyl-4-aminophenyl ether, 2-hydroxyethyl-4-aminophenyl ether, (4-aminophenoxy)acetaldehyde, (4-aminophenoxy)acetic acid, (4-aminophenoxy)methanesulfonic acid, 1-propenyl-4-aminophenyl ether isobutyrate, (2-chloro)-1-propenyl-4-aminophenyl ether, (2-nitro)-1-propenyl-4-aminophenyl ether, (2-amino)-propenyl-4-aminophenyl ether, (2-hydroxy)-1-propenyl-4-aminophenyl ether, N-methyl-p-aminophenol, 3-methyl-4-aminophenol, 2-chloro-4-aminophenol, 3-chloro-4-aminophenol, 2,6-dimethyl-4-aminophenol, 3,5-dimethyl-4-aminophenol, 2,3-dimethyl-4-aminophenol, 2,5-dimethyl-4-aminophenol, 2-hydroxymethyl-4-aminophenol, 3-hydroxymethyl-4-aminophenol, 2,6-dichloro-4-aminophenol, 2,6-dibromo-4-aminophenol and 2-bromo-4-aminophenol.



Specific examples of formula (III) compounds are:

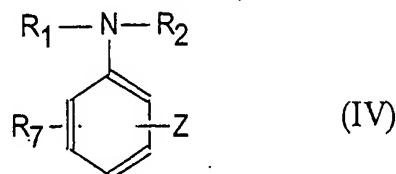
o-hydroxyphenol (catechol), m-hydroxyphenol (resorcinol), p-hydroxyphenol (hydroquinone), 4-methoxyphenol, 2-methoxyphenol, 4-(2-chloroethoxy) phenol, 4-(2-propenoxy) phenol, 4-(3-chloro-2-propenoxy) phenol, 2-chloro-4-hydroxyphenol (2-chlorohydroquinone), 2-nitro-4-hydroxyphenol (2-nitrohydroquinone), 2-amino-4-hydroxyphenol, 1,2,3-trihydroxybenzene (pyrogallol), 2,4-dihydroxybenzaldehyde, 3,4-dihydroxybenzoic acid, 2,4-dihydroxybenzenesulfonic acid, 3-ethyl-4-hydroxyphenol, 3-(2-nitroethyl)-4-hydroxyphenol, 3-(2-propenyl)-4-hydroxyphenol, 3-(3-chloro-2-propenyl)-4-hydroxyphenol, 2-phenyl-4-hydroxyphenol, 2-(4-chlorophenyl)-4-hydroxyphenol, 2-benzyl-4-hydroxyphenol, 2-(2-nitrophenyl)-4-hydroxyphenol, 2-(2-methylphenyl)-4-hydroxyphenol, 2-(2-methyl-4-

chlorophenyl)-4-hydroxyphenol, 3-methoxy-4-hydroxy-benzaldehyde, 2-methoxy-4-(1-propenyl)phenol, 4-hydroxy-3-methoxycinnamic acid, 2,5-dimethoxyaniline, 2-methylresorcinol, alpha naphthol and salts thereof.

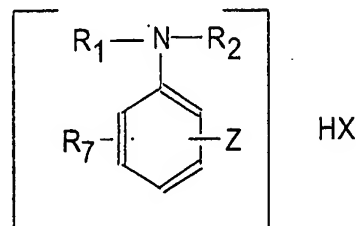
Secondary coupling compounds which are suitable for inclusion in the coloring compositions and processes herein before described include certain aromatic amines and phenols and derivatives thereof which do not produce color singly, but which modify the color, shade or intensity of the colors developed by the primary oxidized dye intermediates. Certain aromatic amines and phenolic compounds, and derivatives thereof, including some aromatic diamines and polyhydric phenols of the types described by formulas (I), (Ia), (Ib), (II) and (III) above, but which are well known in the art not to be suitable primary intermediates, are suitable as couplers herein. Polyhydric alcohols are also suitable for use as couplers herein.

The aromatic amines and phenols and derivatives described above as couplers can also have additional substituents on the aromatic ring, e.g., halogen, aldehyde, carboxylic acid, nitro, sulfonyl and substituted and unsubstituted by hydrocarbon groups, as well as additional substituents on the amino nitrogen, or phenolic oxygen, e.g. substituted and unsubstituted alkyl and aryl groups. Again, peroxide-compatible salts thereof are suitable for use herein.

Examples of aromatic amines, phenols and derivatives thereof are compounds of the general formulas (IV) and (V) below:



OR



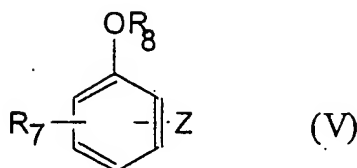
wherein Z is hydrogen, C₁ and C₃ alkyl, halogen (e.g. fluorine, chlorine, bromine or iodine) nitro,



-COOM or SO₃M, (where M is hydrogen or an alkali or alkaline earth metal, ammonium or substituted ammonium wherein one or more hydrogens on the ammonium ion is replaced with a 1 to 3 carbon atom alkyl or hydroxyalkyl radical), wherein R₁ and R₂ are the same or different and are selected from the group consisting of hydrogen, C₁ to C₄ alkyl or alkenyl and C₆ to C₉ aryl, alkaryl or aralkyl and R₇ is hydrogen, C₁ to C₄ unsubstituted or substituted alkyl or alkenyl wherein the substituents are selected from those designated as Z above or C₆ to C₉ unsubstituted or substituted aryl, alkaryl or aralkyl wherein the substituents are selected from those defined as Z above and wherein X is as defined in formula (I).

Specific examples of formula (IV) compounds are:

aniline, p-chloroaniline, p-fluoroaniline, p-nitroaniline, p-aminobenzaldehyde, p-aminobenzoic acid, sodium-p-aminobenzoate, lithium-p-aminobenzoate, calcium di-p-aminobenzoate, ammonium-p-aminobenzoate, trimethylammonium-p-aminobenzoate, tri(2-hydroxyethyl)-p-aminobenzoate, p-aminobenzenesulfonic acid, potassium p-aminobenzenesulfonate, N-methylaniline, N-propyl-N-phenylaniline, N-methyl-N-2-propenylaniline, N-benzylaniline, N-(2-ethylphenyl)aniline, 4-methylaniline, 4-(2-bromoethyl)aniline, 2-(2-nitroethyl)aniline, (4-aminophenyl)acetaldehyde, (4-aminophenyl)acetic acid, 4-(2-propenyl)aniline acetate, 4-(3-bromo-2-propenyl)aniline, 4-phenylaniline chloroacetate, 4-(3-chlorophenyl)aniline, 4-benzylaniline, 4-(4-iodobenzyl)aniline, 4-(3-ethylphenyl)aniline, 4-(2-chloro-4-ethylphenyl)aniline.



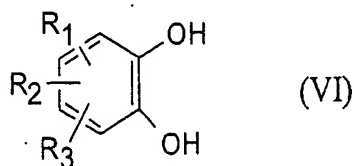
wherein Z and R₇ are defined as in formula (IV) and R₈ is hydrogen or C₁ to C₄ substituted or unsubstituted alkyl or alkenyl wherein the substituents are selected from those defined as Z in formula (IV).

Specific examples of formula (V) compounds are:

phenol, p-chlorophenol, p-nitrophenol, p-hydroxybenzaldehyde, p-hydroxybenzoic acid, p-hydroxybenzenesulfonic acid, ethylphenyl ether, 2-chloroethylphenyl ether, 2-nitroethylphenyl ether, phenoxyacetaldehyde, phenoxyacetic acid, 3-phenoxy-1-propene, 3-phenoxy-2-nitro-1-propene, 3-phenoxy-2-bromo-1-propene, 4-propylphenol, 4-(3-bromopropyl)phenol, 2-(2-nitroethyl)phenol, (4-hydroxyphenyl)acetaldehyde, (4-hydroxyphenyl)acetic acid, 4-(2-propenyl)phenol, 4-phenylphenol, 4-benzylphenol, 4-(3-fluoro-2-propenyl)phenol, 4-(4-chlorobenzyl)phenol, 4-(3-ethylphenyl)phenol, 4-(2-chloro-3-ethylphenyl)phenol, 2,5-xylol, 2,5-diaminopyridine, 2-hydroxy-5-aminopyridine, 2-amino-3-hydroxy pyridine, tetraaminopyrimidine, 1,2,4-trihydroxybenzene, 1,2,4-trihydroxy-5-(C₁-C₆-alkyl)benzene, 1,2,3-trihydroxybenzene, 4-aminoresorcinol, 1,2-dihydroxybenzene, 2-amino-1,4-dihydroxybenzene, 2-amino-4-methoxy-phenol, 2,4-diaminophenol, 3-methoxy-1,2-dihydroxy-benzene, 1,4-dihydroxy-2-(N,N-diethylamino)benzene, 2,5-diamino-4-methoxy-1-hydroxybenzene, 4,6-dimethoxy-3-amino-1-hydroxybenzene, 2,6-dimethyl-4-[N-(p-hydroxyphenyl)amino]-1-hydroxybenzene, 1,5-diamino-2-methyl-4-[N-(p-hydroxyphenyl)amino]benzene and salts thereof.

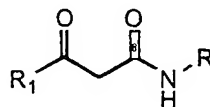
Additional primary intermediates suitable for use herein include catechol species and in particular catechol "dopa" species which includes dopa itself as well as homologs, analogs and derivatives of DOPA. Examples of suitable catechol species include cysteinyl dopa, alpha alkyl dopa having 1 to 4, preferably 1 to 2 carbon atoms in the alkyl group, epinephrine and dopa alkyl esters having 1 to 6, preferably 1 to 2 carbon atoms in the alkyl group.

In general suitable catechols are represented by formula (VI) below:

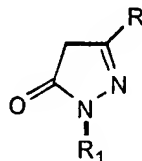


wherein R_1 , R_2 and R_3 , which may be the same or different, are electron donor or acceptor substituents selected from H, lower (C_1 - C_6) alkyl, OH, OR, COOR, NHCOR, CN, COOH, Halogen, NO_2 , CF_3 , SO_3H or NR_4R_5 , with the proviso that only one of the R_1 , R_2 or R_3 can be CN, COOH, halogen, NO_2 , CF_3 or SO_3H ; R_4 and R_5 , which may be the same or different, are H, lower (C_1 - C_6) alkyl or substituted lower (C_1 - C_6) alkyl in which the substituent may be OH, OR, NHCOR₆, NHCONH₂, NHCO₂R₆, NHCSNH₂, CN, COOH, SO_3H , SO_2NR_6 , SO_2R_6 or CO_2R_6 ; R_6 is lower (C_1 - C_6) alkyl, lower (C_1 - C_6) hydroxyalkyl phenyl linked to the nitrogen by an alkylene chain, phenyl or substituted phenyl with the substituent defined as R_1 , and R is C_1 - C_6 alkyl or C_1 - C_6 hydroxyalkyl.

Also included herein are oxidative hair coloring agents of the formula:



wherein: R_1 = substituted or unsubstituted benzene ring, tertiary-butyl, etc.; R = substituted or unsubstituted benzene ring and the formula:



wherein R = aminoalkyl, amidoalkyl, aminobenzene (substituted or unsubstituted), amidobenzene (substituted or unsubstituted), alkyl, substituted or unsubstituted benzene ring; R_1 = substituted or unsubstituted benzene ring.

The primary intermediates can be used herein alone or in combination with other primary intermediates, and one or more can be used in combination with one or more couplers. The choice of primary intermediates and couplers will be determined by the color, shade and intensity of coloration which is desired. There are nineteen preferred primary intermediates and couplers which can be used herein, singly or in combination, to provide dyes having a variety

of shades ranging from ash blonde to black; these are: pyrogallol, resorcinol, p-toluenediamine, p-phenylenediamine, o-phenylenediamine, m-phenylenediamine, o-aminophenol, p-aminophenol, 4-amino-2-nitrophenol, nitro-p-phenylenediamine, N-phenyl-p-phenylenediamine, m-aminophenol, 2-amino-3-hydroxypyridine, 1-naphthol, N,N bis (2-hydroxyethyl)p-phenylenediamine, 4-amino-2-hydroxytoluene, 1,5-dihydroxynaphthalene, 2-methyl resorcinol and 2,4-diaminoanisole. These can be used in the molecular form or in the form of peroxide-compatible salts, as detailed above.

For example low intensity colors such as natural blond to light brown hair shades generally comprise from about 0.001% to about 5%, preferably from about 0.1% to about 2%, more preferably from about 0.2% to about 1% by weight of coloring composition of total oxidative dyeing agents and may be achieved by the combination of primary intermediates such as 1,4-diamino-benzene, 2,5-diamino toluene, 2,5-diamino-anisole, 4-aminophenol, 2,5-diamino-benzyl alcohol and 2-(2',5'-diamino)phenyl-ethanol with couplers such as resorcinol, 2-methyl resorcinol or 4-chloro resorcinol.

Similarly combination of the above primary intermediates with couplers, such as, 5-amino-2-methyl phenol and 1,3-diamino-benzene derivatives such as 2,4-diamino-anisole at levels of from about 0.5% to about 1% of total dyeing agents can lead to medium intensity red colors. High intensity colors such as blue to blue-violet hair shades can be produced by the combination of the above primary intermediates with couplers such as 1,3-diamino-benzene or its derivatives such as 2,5-diamino-toluene at levels of from about 1% to about 6% by weight of composition of total dyeing agents. Black hair colors can be obtained by combining the aforementioned primary intermediates with couplers such as 1,3-diaminobenzene or its derivatives

Non-oxidative and other dyes

The hair coloring compositions of the present invention may, in addition to or instead of an oxidative hair coloring agent, include non-oxidative and other dye materials. Optional non-oxidative and other dyes suitable for use in the hair coloring compositions and processes according to the present invention include both semi-permanent, temporary and other dyes. Non-oxidative dyes as defined herein include the so-called 'direct action dyes', metallic dyes, metal chelate dyes, fibre reactive dyes and other synthetic and natural dyes. Various types of

non-oxidative dyes are detailed in: 'Chemical and Physical Behaviour of Human Hair' 3rd Ed. by Clarence Robbins (pp250-259); 'The Chemistry and Manufacture of Cosmetics'. Volume IV. 2nd Ed. Maison G. De Navarre at chapter 45 by G.S. Kass (pp841-920); 'cosmetics: Science and Technology' 2nd Ed., Vol. II Balsam Sagarin, Chapter 23 by F.E. Wall (pp 279-343); 'The Science of Hair Care' edited by C. Zviak, Chapter 7 (pp 235-261) and 'Hair Dyes', J.C. Johnson, Noyes Data Corp., Park Ridge, U.S.A. (1973), (pp 3-91 and 113-139).

Direct action dyes which do not require an oxidative effect in order to develop the color, are also designated hair tints and have long been known in the art. They are usually applied to the hair in a base matrix which includes surfactant material. Direct action dyes include nitro dyes such as the derivatives of nitroamino benzene or nitroaminophenol; disperse dyes such as nitroaryl amines, aminoanthraquinones or azo dyes; anthraquinone dyes, naphthoquinone dyes; basic dyes such as Acridine Orange C.I. 46005. In the case of direct dyes, these are preferably used in combination with an oxidative hair colouring agent in the compositions herein.

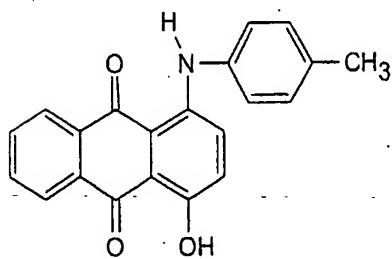
Nitrodyes are added to dyeing compositions to enhance the colour of the colorant and to add suitable aesthetic colour to the dye mixture prior to application.

Further examples of direct action dyes include the Arianor dyes basic brown 17, C.I.(color index) - no. 12,251; basic red 76, C.I. - 12,245; basic brown 16, C.I. - 12,250; basic yellow 57, C.I. - 12,719 and basic blue 99, C.I. - 56,059 and further direct action dyes such as acid yellow 1, C.I. - 10,316 (D&C yellow no.7); acid yellow 9, C.I. - 13,015; basic violet C.I. - 45,170; disperse yellow 3, C.I. - 11,855; basic yellow 57, C.I. - 12,719; disperse yellow 1, C.I. - 10,345; basic violet 1, C.I. - 42,535, basic violet 3, C.I. - 42,555; greenish blue, C.I. - 42090 (FD&C Blue no.1); yellowish red, C.I.-14700 (FD&C red no.4); yellow, C.I.19140 (FD&C yellow no5); yellowish orange, C.I.15985 (FD&C yellow no.6); bluish green, C.I.42053 (FD&C green no.3); yellowish red, C.I.16035 (FD&C red no.40); bluish green, C.I.61570 (D&C green no.3); orange, C.I.45370 (D&C orange no.5); red, C.I.15850 (D&C red no.6); bluish red, C.I.15850 (D&C red no.7); slight bluish red, C.I.45380 (D&C red no.22); bluish red, C.I.45410 (D&C red no.28); bluish red, C.I.73360 (D&C red no.30); reddishpurple, C.I.17200 (D&C red no.33); dirty blue red, C.I.15880 (D&C red no.34); bright yellow red, C.I.12085 (D&C red no.36); bright orange, C.I.15510 (D&C orange no.4); greenish yellow, C.I.47005 (D&C yellow no.10); bluish green, C.I.59040 (D&C green no.8); bluish violet, C.I.60730 (Ext. D&C violet no.2); greenish yellow, C.I.10316 (Ext. D&C yellow no.7);

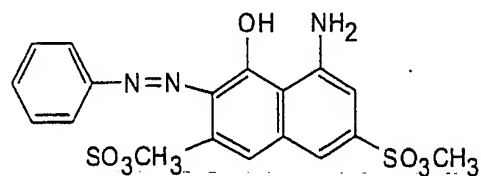
Fibre reactive dyes include the Procion (RTM), Drimarene (RTM), Cibacron (RTM), Levafix (RTM) and Remazol (RTM) dyes available from ICI, Sandoz, Ciba-Geigy, Bayer and Hoechst respectively.

Natural dyes and vegetable dyes as defined herein include henna (*Lawsonia alba*), camomile (*Matricaria chamomila* or *Anthemis nobilis*), indigo, logwood and walnut hull extract.

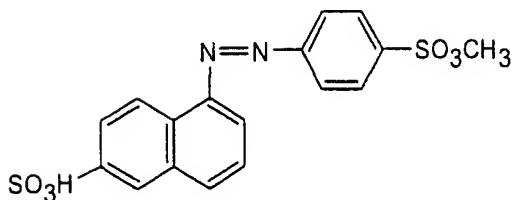
Temporary hair dyes, or hair coloring rinses, are generally comprised of dye molecules which are too large to diffuse into the hair shaft and which act on the exterior of the hair. They are usually applied via a leave-in procedure in which the dye solution is allowed to dry on the hair surface. As such these dyes are typically less resistant to the effects of washing and cleaning the hair with surface active agents and are washed off of the hair with relative ease. Any temporary hair dye may suitably be used in the compositions of the invention and examples of preferred temporary hair dyes are illustrated below. Temporary dyes are preferably used together with an oxidative colouring agent in the composition herein.



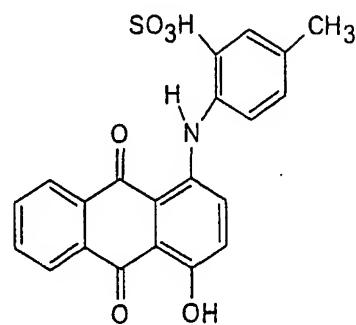
Violet



Red

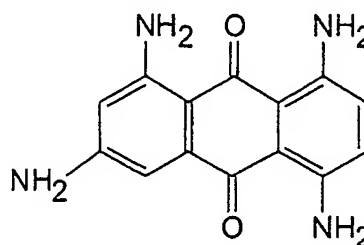
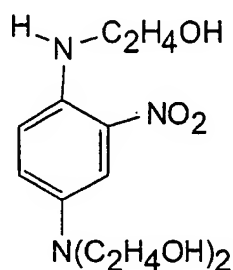


Yellow

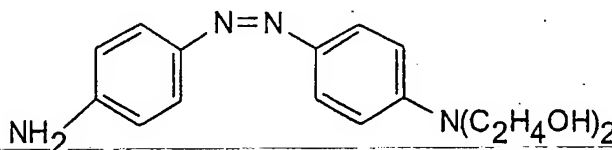
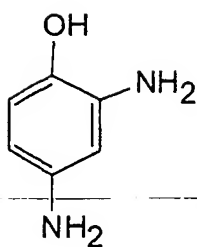


Blue-Violet

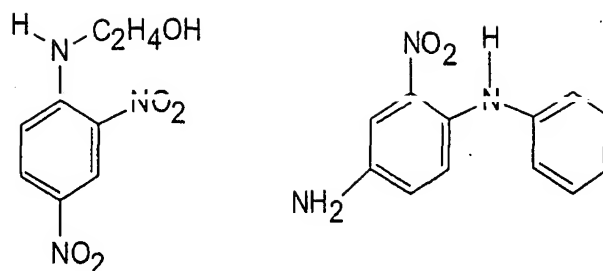
Semi-permanent hair dyes are dyes which are generally smaller in size and effect to temporary hair rinses but are generally larger than permanent (oxidative) dyes. Typically, semi-permanent dyes act in a similar manner to oxidative dyes in that they have the potential to diffuse into the hair shaft. However, semi-permanent dyes are generally smaller in size than the aforementioned conjugated oxidative dye molecules and as such are pre-disposed to gradual diffusion out of the hair again. Simple hair washing and cleaning action will encourage this process and in general semi-permanent dyes are largely washed out of the hair after about 5 to 8 washes. Any semi-permanent dye system may be suitably used in the compositions of the present invention. Suitable semi-permanent dyes for use in the compositions of the present invention are HC Blue 2, HC Yellow 4, HC Red 3, Disperse Violet 4, Disperse Black 9, HC Blue 7, HC Yellow 2, Disperse Blue 3, Disperse violet 1 and mixtures thereof. Examples of semi-permanent dyes are illustrated below:



BlueBlue



YellowYellow



RedRed

Typical semi-permanent dye systems incorporate mixtures of both large and small color molecules. As the size of the hair is not uniform from root to tip the small molecules will diffuse both at the root and tip, but will not be retained within the tip, while the larger molecules will be generally only be able to diffuse into the ends of the hair. This combination of dye molecule size is used to help give consistent color results from the root to the tip of the hair both during the initial dyeing process and during subsequent washing.

Oxidising Agents

As discussed above, oxidising agents such as hydrogen peroxide may also be classed herein as a hair colour altering agent. Therefore the compositions herein can contain an oxidising agent as the sole hair colour altering agent. This is particularly the case when it is desired to produce blond shades. When other shades are required however it is also necessary to have another hair colouring agent present, for example, an oxidative hair colouring agent.

The compositions herein preferably comprise at least one oxidising agent, which may be an inorganic or organic oxidising agent. The oxidising agent is preferably present at a level of from about 0.01% to about 10%, preferably from about 0.01% to about 6%, more preferably from about 1% to about 4% by weight of composition.

Inorganic Oxidising Agents

A preferred oxidising agent for use herein is an inorganic peroxygen oxidising agent.

The inorganic peroxygen oxidising agent should be safe and effective for use in the compositions herein. Preferably, the inorganic peroxygen oxidising agents suitable for use herein will be soluble in the compositions according to the present invention when in liquid form or in the form intended to be used. Preferably, inorganic peroxygen oxidising agents suitable for use herein will be water-soluble. Water soluble oxidising agents as defined herein means agents which have a solubility to the extent of about 10g in 1000ml of deionised water at 25°C ("Chemistry" C. E. Mortimer. 5th Edn. p277).

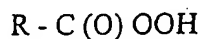
The inorganic peroxygen oxidising agents useful herein are generally inorganic peroxygen materials capable of yielding peroxide in an aqueous solution. Inorganic peroxygen oxidising agents are well known in the art and include hydrogen peroxide, inorganic alkali metal peroxides such as sodium periodate, sodium perbromate and sodium peroxide, and inorganic perhydrate salt oxidising compounds, such as the alkali metal salts of perborates, percarbonates, perphosphates, persilicates, persulphates and the like. These inorganic perhydrate salts may be incorporated as monohydrates, tetrahydrates etc. Mixtures of two or more of such inorganic peroxygen oxidising agents can be used if desired. While alkali metal bromates and iodates are suitable for use herein the bromates are preferred. Highly preferred for use in the compositions according to the present invention is hydrogen peroxide.

In preferred compositions herein the inorganic peroxygen oxidising agent is present at a level of from about 0.01% to less than about 6%, preferably from about 0.01% to about 4%, more preferably from about 1% to about 4%, more preferably from about 2% to about 3% by weight of composition.

Preformed organic peroxyacid

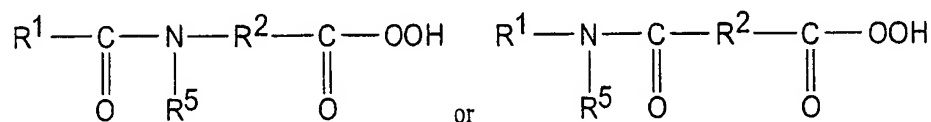
The compositions herein may instead or in addition to the inorganic peroxygen oxidising agent(s), comprise one or more preformed organic peroxyacid oxidising agents.

Suitable organic peroxyacid oxidising agents for use in the coloring compositions according to the present invention have the general formula:



wherein R is selected from saturated or unsaturated, substituted or unsubstituted, straight or branched chain, alkyl, aryl or alkaryl groups with from 1 to 14 carbon atoms.

A class of organic peroxyacid compounds suitable for use herein are the amide substituted compounds of the following general formulae:



wherein R¹ is, a saturated or unsaturated alkyl or alkaryl group, or an aryl group, having from 1 to 14 carbon atoms, R² is, a saturated or unsaturated alkyl or alkaryl group, or an aryl group, having from 1 to 14 carbon atoms, and R⁵ is H or, a saturated or unsaturated alkyl or alkaryl group, or an aryl group, having from 1 to 10 carbon atoms. Amide substituted organic peroxyacid compounds of this type are described in EP-A-0,170,386.

Other suitable organic peroxyacid oxidising agents include peracetic, permanganic, nonylamidoperoxycaproic acid (NAPCA), perbenzoic, m-chloroperbenzoic, di-peroxy-isophthalic, mono-peroxyphthalic, peroxyauric, hexanesulphonyl peroxy propionic, N,N-phthaloylamino peroxyacetic, monoper succinic, nonanoyloxybenzoic, dodecanedioyl-monoperoxybenzoic, nonylamide of peroxyadipic acid, diacyl and tetraacylperoxides, especially diperoxydodecanedioic acid, diperoxytetradecanedioic acid and diperoxyhexadecanedioic acid and derivatives thereof. Mono- and diperazelaic acid, mono- and diperbrassylic acid and N-phthaloylamino-peroxycaproic acid and derivatives thereof are also suitable for use herein.

The preformed organic peroxyacid oxidising agents should be safe and effective for use in the compositions herein. Preferably, the preformed organic peroxyacid oxidising agents suitable for use herein will be soluble in the compositions according to the present invention when in liquid form and in the form intended to be used. Preferably, organic peroxyacid oxidising agents suitable for use herein will be water-soluble. Water-soluble preformed organic peroxyacid oxidising agents as defined herein means agents which have a solubility to the extent of about 10g in 1000ml of deionised water at 25°C ("Chemistry" C. E. Mortimer. 5th Edn. p277).

The preferred peroxyacid materials suitable for use herein are selected from peracetic and permanoic acids and mixtures thereof.

The preformed organic peroxyacid oxidising agent, where present, is preferably present at a level of from about 0.01% to about 8%, more preferably from about 0.1% to about 6%, most preferably from about 0.2% to about 4%, and especially from about 0.3% to about 3% by weight of the hair coloring composition.

When both an inorganic peroxygen oxidising agent and a preformed organic peroxy acid are present in the compositions herein, the weight ratio of the inorganic peroxygen oxidising agent to the preformed organic peroxy acid is preferably in the range of from about 0.0125:1 to about 500:1, more preferably from about 0.0125:1 to about 50:1.

In addition to the inorganic peroxygen oxidising agents and the preformed organic peroxyacid oxidising agents suitable for use herein, the compositions according to the present invention may optionally comprise additional organic peroxides such as urea peroxide, melamine peroxide and mixtures thereof. The level of organic peroxide, where present, is from about 0.01% to about 3%, preferably from about 0.01% to about 2%, more preferably from about 0.1% to about 1.5% and most preferably from about 0.2% to about 1% by weight of composition.

Conditioning Agent

The hair colour altering composition preferably comprises one or more hair conditioning agents. The conditioning agent herein can be any conditioning agent suitable for use in conditioning hair

The conditioning agent is preferably present at a level of from about 0.1% to about 25%, preferably from about 1% to about 20%, more preferably from about 5% to about 20% and especially from about 5% to about 15%, by weight of the hair colouring and conditioning composition.

Suitable conditioning agents for use herein include, but are not limited to, cationic surfactants, cationic polymers, insoluble silicones, non-volatile hydrocarbons, saturated C14-C22 straight chain fatty alcohols, non-volatile hydrocarbon esters, and mixtures thereof. Other suitable

conditioning agents are disclosed in WO95/20939 and WO96/32919 which are incorporated herein by reference.

Preferred conditioning agents for use herein include cationic surfactants, cationic polymers, insoluble silicone conditioning agents and saturated C14-C22 straight chain fatty alcohols and mixtures thereof. Especially preferred for use herein is a mixture of cationic polymer, non-volatile silicone and C14-C22 straight chain fatty alcohols.

When present, the insoluble silicone conditioning agents are present at a level of from about 0.1 to 10%, preferably from about 0.1% to about 5%, more preferably from about 1% to about 3% by weight of composition. Suitable insoluble silicones include polyalkyl siloxanes, polyaryl siloxanes, polyalkylaryl siloxanes, polyether siloxane copolymers, and mixtures thereof. The silicone conditioning agent will preferably be non-volatile. As used herein the term "non-volatile" shall mean that the material has a boiling point of at least about 260°C, preferably at least about 275°C, more preferably at least about 300°C. Such materials exhibit very low or no significant vapour pressure at ambient conditions. The term "silicone fluid" shall mean flowable silicone materials having a viscosity of less than 1,000,000 centistokes at 25°C. The term "silicone gum" shall mean flowable silicone materials having a viscosity of 1,000,000 centistokes at 25°C or greater. The viscosity can be measured by a glass capillary viscometer as in Dow Corning Corporate Test Method CTM0004, July 20, 1920, or equivalent.

A preferred silicone material for use herein is a polydimethyl siloxane. These silicones are available for example from the General Electric Company in their Viscasil and SF96 series, and from Dow Corning in their Dow Corning 200 series.

Other suitable insoluble silicones for use herein are disclosed in WO96/32919 which is incorporated herein by reference.

When present, the cationic polymers are present at a level of from about 0.1 to 10%, preferably from about 0.1% to about 5%, more preferably from about 1% to about 3% by weight of composition. Suitable cationic polymers for use herein are disclosed in WO96/32919 which is incorporated herein by reference.

When present, the fatty alcohols are present at a level of from about 0.1% to about 20%, preferably from about 1% to about 15% and more preferably from about 3% to about 10% by weight of composition. Preferred fatty alcohols for use herein are cetyl alcohol and stearyl alcohol and mixtures thereof.

The coloring compositions used in the methods of the present invention can be formulated over a wide pH range, eg. from about 2 to about 13, but from the viewpoint of providing compositions with reduced damage and reduced skin staining, the compositions are preferably formulated at low pH, preferably preferably have a pH in the range of from about 2 to about 7, preferably from about 2.5 to about 6, more preferably from about 3 to about 6, even more preferably from about 3.5 to about 5.5, and especially from about 4 to about 5.5. The compositions herein can also be formulated at high pH, preferably in a pH range of from about 8 to about 12, more preferably from about 9 to about 11.

The compositions may contain one or more optional buffering agents and/or hair swelling agents (HSAs). Several different pH modifiers can be used to adjust the pH of the final composition or any constituent part thereof. However, preferred compositions herein are substantially free of additional buffering agents, and hair swelling agents, i.e. they comprise less than about 1%, preferably less than about 0.5%, more preferably less than about 0.1% by weight of such agents.

This pH adjustment can be effected by using well known acidifying agents in the field of treating keratinous fibres, and in particular human hair, such as inorganic and organic acids such as hydrochloric acid, tartaric acid, citric acid, succinic acid, phosphoric acid and carboxylic or sulphonic acids such as ascorbic acid, acetic acid, lactic acid, sulphuric acid, formic acid, ammonium sulphate and sodium dihydrogenphosphate /phosphoric acid, disodium hydrogenphosphate /phosphoric acid, potassium chloride /hydrochloric acid, potassium dihydrogen phthalate/ hydrochloric acid, sodium citrate / hydrochloric acid, potassium dihydrogen citrate /hydrochloric acid, potassium dihydrogencitrate/ citric acid, sodium citrate / citric acid, sodium tartarate/ tartaric acid, sodium lactate/ lactic acid, sodium acetate/ acetic acid, disodium hydrogenphosphate/ citric acid and sodium chloride/ glycine / hydrochloric acid, succinic acid and mixtures thereof.

Examples of alkaline buffering agents are ammonium hydroxide, ethylamine, dipropylamine, triethylamine and alkanediamines such as 1,3-diaminopropane, anhydrous alkaline alkanolamines such as, mono or di- ethanolamine, preferably those which are completely substituted on the amine group such as dimethylaminoethanol, polyalkylene polyamines such as diethylenetriamine or a heterocyclic amine such as morpholine as well as the hydroxides of alkali metals, such as sodium and potassium hydroxide, hydroxides of alkali earth metals, such as magnesium and calcium hydroxide, basic amino acids such as L-arginine, lysine, alanine, leucine, iso-leucine, oxylysine and histidine and alkanolamines such as dimethylaminoethanol and aminoalkylpropanediol and mixtures thereof. Also suitable for use herein are compounds other than ammonium carbonate or ammonium carbamate that form HCO_3^- by dissociation in water (hereinafter referred to as 'ion forming compounds'). Examples of suitable ion forming compounds are Na_2CO_3 , NaHCO_3 , K_2CO_3 , NH_4HCO_3 , CaCO_3 and $\text{Ca}(\text{HCO}_3)_2$ and mixtures thereof.

The hair colour altering compositions herein, may, as will be described later herein, comprise a final composition containing a hair coloring agent and a conditioning agent which have been admixed prior to application to the hair or a may comprise single component system. As such, the compositions herein may comprise coloring kits of a number of separate components.

In oxidising and coloring kits comprising a portion of inorganic peroxygen oxidising agent, such as hydrogen peroxide, which may be present in either solid or liquid form, a buffering agent solution can be used to stabilise hydrogen peroxide. Since hydrogen peroxide is stable in the pH range from 2 to 4, it is preferable to use a buffering agent having a pH within this range. Dilute acids are suitable hydrogen peroxide buffering agents.

Catalyst

The coloring compositions herein may optionally contain a transition metal containing catalyst for the inorganic peroxygen oxidising agents and the, optional, preformed peroxy acid oxidising agent(s). Suitable catalysts for use herein are disclosed in WO98/27945 which is incorporated herein by reference.

Heavy metal ion sequestrant

The coloring compositions herein may contain as an optional component a heavy metal ion sequestrant. By heavy metal ion sequestrant it is meant herein components which act to sequester (chelate or scavenge) heavy metal ions. These components may also have calcium and magnesium chelation capacity, but preferentially they show selectivity to binding heavy metal ions such as iron, manganese and copper. Such sequestering agents are valuable in hair coloring compositions as herein described for the delivery of controlled oxidising action as well as for the provision of good storage stability of the hair coloring products.

Heavy metal ion sequestrants are generally present at a level of from about 0.005% to about 20%, preferably from about 0.01% to about 10%, more preferably from about 0.05% to about 2% by weight of the compositions.

Suitable sequestering agents are disclosed in WO98/27945 which is incorporated herein by reference in its entirety.

Thickeners

The coloring compositions of the present invention may additionally include a thickener at a level of from about 0.05% to about 20%, preferably from about 0.1% to about 10%, more preferably from about 0.5% to about 5% by weight. Thickening agents suitable for use in the compositions herein are selected from oleic acid, cetyl alcohol, oleyl alcohol, sodium chloride, cetearyl alcohol, stearyl alcohol, synthetic thickeners such as Carbopol, Aculyn and Acrosyl and mixtures thereof. Preferred thickeners for use herein are Aculyn 22 (RTM), steareth-20 methacrylate copolymer; Aculyn 44 (RTM), polyurethane resin and Acusol 830 (RTM), acrylates copolymer which are available from Rohm and Haas, Philadelphia, PA, USA. Additional thickening agents suitable for use herein include sodium alginate or gum arabic, or cellulose derivatives, such as methyl cellulose or the sodium salt of carboxymethylcellulose or acrylic polymers.

Diluent

Water is the preferred diluent for the compositions according to the present invention. However, the compositions according to the present invention may include one or more solvents as additional diluent materials. Generally, solvents suitable for use in the coloring compositions of the present invention are selected to be miscible with water and innocuous to the skin. Solvents suitable for use as additional diluents herein include C₁-C₂₀ mono- or polyhydric alcohols and their ethers, glycerine, with monohydric and dihydric alcohols and their ethers preferred. In these compounds, alcoholic residues containing 2 to 10 carbon atoms are

preferred. Thus, a preferred group includes ethanol, isopropanol, n-propanol, butanol, propylene glycol, ethylene glycol monoethyl ether, and mixtures thereof. Water is the preferred principal diluent in the compositions according to the present invention. Principal diluent, as defined herein, means, that the level of water present is higher than the total level of any other diluents.

The diluent is present at a level preferably of from about 5% to about 99.98%, preferably from about 15% to about 99.5%, more preferably at least from about 30% to about 99%, and especially from about 50% to about 98% by weight of the compositions herein.

Enzyme

A further additional material useful in the hair coloring compositions herein is one or more enzymes. Suitable enzymatic materials include the commercially available lipases, cutinases, amylases, neutral and alkaline proteases, esterases, cellulases, pectinases, lactases and peroxidases conventionally incorporated into detergent compositions. Suitable enzymes are discussed in US Patents 3,519,570 and 3,533,139 and in WO98/27945 which is incorporated herein by reference in its entirety.

Surfactant Materials

The compositions herein can additionally contain a surfactant system. Suitable surfactants for inclusion in the compositions of the invention generally have a lipophilic chain length of from about 8 to about 22 carbon atoms and can be selected from anionic, cationic, nonionic, amphoteric, zwitterionic surfactants and mixtures thereof. Suitable surfactants for use herein are disclosed in WO98/27945 which is incorporated herein by reference in its entirety. For preferred methods herein, it is preferable that the hair colour altering composition comprises less than about 10% surfactant, preferably less than about 5% surfactant. It is also preferable that the hair colour altering compositions comprise less than about 5% anionic surfactant.

Optional Materials

A number of additional optional materials can be added to the coloring compositions herein described each at a level of from about 0.001% to about 5%, preferably from about 0.01% to about 3%, more preferably from about 0.05% to about 2% by weight of composition. Such materials include proteins and polypeptides and derivatives thereof; water-soluble or

solubilizable preservatives such as DMDM Hydantoin, Germall 115, methyl, ethyl, propyl and butyl esters of hydroxybenzoic acid, EDTA, Euxyl (RTM) K400, natural preservatives such as benzyl alcohol, potassium sorbate and bisabolol, benzoic acid, sodium benzoate and 2-phenoxyethanol; antioxidants such as sodium sulphite, hydroquinone, sodium bisulphite, sodium metabisulphite and thyoglycolic acid, sodium dithionite, erythroic acid and other mercaptans; dye removers such as oxalic acid, sulphated castor oil, salicylic acid and sodium thiosulphate; H₂O₂ stabilisers such as tin compounds such as sodium stannate, stannic hydroxide and stannous octoate, acetanilide, phenacetin colloidal silica such as magnesium silicate, oxyquinoline sulphate, sodium phosphate, and tetrasodium pyrophosphate; and *p*-hydroxybenzoates; moisturising agents such as hyaluronic acid, chitin, and starch-grafted sodium polyacrylates such as Sanwet (RTM) IM-1000, IM-1500 and IM-2500 available from Celanese Superabsorbent Materials, Portsmouth, VA, USA and described in US-A-4,076,663 as well as methyl cellulose, starch, higher fatty alcohols, paraffin oils, fatty acids and the like; solvents; anti-bacterial agents such as Oxeco (phenoxy isopropanol); low temperature phase modifiers such as ammonium ion sources (e.g. NH₄ Cl); viscosity control agents such as magnesium sulfate and other electrolytes; quaternary amine compounds such as distearyl-, dilauryl-, di-hydrogenated beef tallow-, dimethyl ammonium chloride, dicetyldiethyl ammoniummethylsulphate, ditallowdimethyl ammonium methylsulphate, disoya dimethyl ammonium chloride and dicoco dimethyl ammonium chloride; hair conditioning agents such as silicones, higher alcohols, cationic polymers and the like; enzyme stabilisers such as water soluble sources of calcium or borate species; colouring agents; TiO₂ and TiO₂-coated mica; perfumes and perfume solubilizers; and zeolites such as Valfour BV400 and derivatives thereof and Ca²⁺/Mg²⁺ sequestrants such as polycarboxylates, amino polycarboxylates, polyphosphonates, amino polyphosphonates etc. and water softening agents such as sodium citrate.

Method of use

It is important that dyeing compositions be in a form which is easy and convenient to prepare and use by the consumer, since the oxidising agent must remain in contact with the hair for a certain period of time and not run or drip off of the hair, possibly causing eye or skin irritation.

To address the above, the coloring compositions can be provided in both a single pack or in kit form as separately packaged components to maintain stability, and, if so desired, either

mixed by the user immediately prior to application to the hair, or mixed and stored for future use, or mixed and partly used and the remainder stored for future use.

As hereinbefore described, the compositions may be used by the consumer as a single component package. Such a single pack would comprise a single composition containing the hair coloring agent and the hair conditioning agent. The composition would be applied directly to the hair by the consumer without the need for any pretreatments or mixing thereby providing a simple, fast, easy to use, 'no-mess' hair colouring and conditioning system. A further advantage of such a single component system is that it could be stored and re-used i.e., a single package could contain enough colouring composition for several applications over time. In addition, the compositions may be dispensed from a pack having dual chambers, each chamber comprising a single component, wherein the single components are intended to be mixed, either within the pack or outside the pack to form a homogeneous composition which can be applied to the hair.

The colouring and conditioning compositions herein are preferably applied to the hair like a conventional conditioning rinse composition and rinsed from the hair after use. The colouring and conditioning compositions are thereby easy and convenient to use in the shower. The colouring and conditioning compositions are preferably applied to the hair for periods of from 0.5 minutes to 15 minutes depending upon the degree of coloring required. A preferred time is from 0.5 minutes and 5 minutes, preferably 1 minute to about 5 minutes, more preferably from about 1 minute to about 3 minutes. The coloring compositions herein are preferably applied to wet hair after the hair has been shampooed.

Kits

According to the present invention there is also provided a hair coloring kit wherein the kit comprises (a) a hair colour altering composition and (b) a set of instructions for using the hair colour altering composition according to a particular method wherein the method comprises the steps of (a) applying to hair a hair colour altering composition, (b) leaving the hair colour altering composition on the hair for from about 0.5 to 15 minutes and then (c) optionally, rinsing the hair colour altering composition from the hair, wherein steps (a), (b) and (c) are repeated from about once a month to about 3 times a day.

Preferred kits comprise a package which contains two or more separate components. In preferred embodiments the kit components are admixed to form a colouring and conditioning composition prior to application to the hair. In alternative embodiments, the individual components can be applied separately to the hair in a sequential manner.

A preferred kit herein comprises a package comprising at least two components, a first component containing a combination of an oxidative and/or non-oxidative hair coloring agent and a conditioning agent and a second component comprising an oxidising agent and a conditioning agent. The components can either be mixed by the user immediately prior to application to the hair or can be applied separately. The components can also be mixed and the resulting composition can be stored for future use or part of the resulting composition can be used and the rest of the composition stored for future use. In one embodiment of the present invention the oxidising component comprises a stabilised cream comprising an inorganic peroxygen oxidising agent, most generally hydrogen peroxide in an amount such that the final concentration of the coloring composition for use on the hair is from about 0.05% to about 6% by weight and additional agents as herein before described.

In kits comprising two or more components, these components may be packaged separately or may be packaged in a single package having several chambers, one chamber for each separate component.

A preferred pack herein is a pack having two chambers, one chamber comprising a first component comprising a hair colouring agent and a second chamber comprising a second component comprising an oxidising agent. Either or both of the second components may contain a conditioning agent, provided at least one of the components contains a conditioning agent. The two components can be mixed either outside the pack, for example, by hand, or within the pack, for example by a mechanical means of mixing. It is preferable that the two components are mixed sufficiently in order to provide a homogeneous hair colouring and conditioning composition for application to the hair. Such a pack provides a product which is easy and convenient to use in the shower. The compositions herein can also be packaged within blister packs and sachets.

In some embodiments the kit may additionally comprise an initial colouring composition suitable for providing an initial colour to hair before the use of the hair colour altering composition. The

consumer applies colour initially using the initial colouring composition and maintains the colour over the subsequent weeks by the use of the hair colour altering composition. Generally the initial colouring composition and hair colour altering composition are of substantially the same shade.

The present invention is represented by the following non-limiting examples. In the examples, all concentrations are on a 100% active basis and all percentages are by weight unless otherwise stated and the abbreviations have the following designations.

Examples I - XV

Examples I-XV are compositions containing oxidative hair colouring agents. Any of these compositions can be mixed with the composition of Example XVI in a 1:1 ratio in order to provide a hair colouring and conditioning composition used in the methods according to the present invention.

<u>Ingredient</u>	<u>I</u>	<u>II</u>	<u>III</u>	<u>IV</u>	<u>V</u>	<u>VI</u>	<u>VII</u>	<u>VIII</u>
Dye Premix:								
Demineralized Water	45.9	45.77	45.83	44.6	44.56	43.9	44.91	43.31
Citric Acid	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7
Tetrasodium EDTA	0.19	0.19	0.19	0.19	0.19	0.19	0.19	0.19
Sodium Sulphite	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
pPD ¹	0	0.1	0	0.24	0	0.4	0.332	0.2
mPD sulphate ²	0	0.001	0	0	0	0	0	0
pAP ³	0	0.012	0	0.27	0.75	0.9	0.332	1.498
2A3HP ⁴	0	0	0	0.6	0.6	0.6	0	0.6
mAP ⁵	0	0.012	0	0	0	0.1	0	0
resorcinol	0	0	0	0	0	0	0	0
4A2HT ⁶	0	0.006	0.04	0	0	0	0	0
o-AP ⁷	0	0	0.04	0	0	0	0.332	0
32% NaOH	0	0	0	0	0	0	0	0
Ascorbic Acid	0	0	0	0.2	0	0	0	0.3

Dye Wash Water:

Water	8	8	8	8	8	8	8	8
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Emulsion Base:

Water	29.77	29.77	29.77	29.77	29.77	29.77	29.77	29.77
Ceteareth-25	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Cetyl Alcohol	2.25	2.25	2.25	2.25	2.25	2.25	2.25	2.25
Stearyl Alcohol	2.25	2.25	2.25	2.25	2.25	2.25	2.25	2.25
Sodium Benzoate	0.09	0.09	0.09	0.09	0.09	0.09	0.09	0.09
Phenoxyethanol	0.108	0.108	0.108	0.108	0.108	0.108	0.108	0.108
Tetrasodium EDTA	0.036	0.036	0.036	0.036	0.036	0.036	0.036	0.036

pH adjusters:

Water	to 100	to 100	to 100	to 100	to 100	to 100	to 100	to 100
50% citric acid 4	0	0	0	0	0	0	0	
32% NaOH	0	1.8	2	1.5	0.7	0.5	1.75	0.467

<u>Ingredient</u>	<u>IX</u>	<u>X</u>	<u>XI</u>	<u>XII</u>	<u>XIII</u>	<u>XIV</u>	<u>XV</u>
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Dye Premix:

Demineralized Water	43.31	42.21	43.81	42.51	41.38	43.84	38.45
Citric Acid	1.7	1.7	1.7	1.7	1.7	1.7	1.7
Tetrasodium EDTA	0.19	0.19	0.19	0.19	0.19	0.19	0.19
Sodium Sulphite	0.2	0.2	0.2	0.2	0.2	0.2	0.2
pPD ¹	0.8	0.6	0	0.8	1.9	0.95	2
mPD sulphate ²	0	0	0	0	0	0	0.4
pAP ³	0.6	1.498	1.498	1.498	0.54	0.27	0
2A3HP ⁴	0	0	0	0	0.44	0.22	0
mAP ⁵	0	0.6	0.6	0.5	0.048	0.024	0
resorcinol	0	0	0	0	0	0	0.45
4A2HT ⁶	0	0	0	0	0	0	0
o-AP ⁷	0	0	0	0	0	0	0
32% NaOH	0	0	0	0	0	0	3.003
Ascorbic Acid	0.6	1	0	0.6	1.6	0.6	1.6

Dye Wash Water:

Water	8	8	8	8	8	8	8
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Emulsion Base:

Water	29.77	29.77	29.77	29.77	29.77	29.77	29.77
Cetareth-25	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Cetyl Alcohol	2.25	2.25	2.25	2.25	2.25	2.25	2.25
Stearyl Alcohol	2.25	2.25	2.25	2.25	2.25	2.25	2.25
Sodium Benzoate	0.09	0.09	0.09	0.09	0.09	0.09	0.09
Phenoxyethanol	0.108	0.108	0.108	0.108	0.108	0.108	0.108
Tetrasodium EDTA	0.036	0.036	0.036	0.036	0.036	0.036	0.036

pH adjusters:

Water	to 100	to 100	to 100	to 100	to 100	to 100	to 100
50% citric acid 0	0	0	0	0	0	0	
32% NaOH	1.8	1.5	0.5	1.6	3.7	1.1	2

1. paraphenylenediamine 2HCl
2. metaphenylenediamine sulphate
3. para-aminophenol
4. 2-amino-3-hydroxypyridine
5. meta-aminophenol
6. 4-amino-2-hydroxytoluene
7. ortho-aminophenol

The compositions of Examples of I-XV are prepared as follows:

The dye premix is prepared by adding to a vessel with stirring the deionised water, sodium sulphite, tetrasodium EDTA, ammonium acetate and dipropylene glycol. The dye materials are then added to the vessel and mixed until dissolved, with heating if necessary. When fully dissolved, the solution is cooled to room temperature, followed by addition of ascorbic acid.

The pH premix is prepared by mixing together in a vessel the sodium hydroxide and deionised water.

The emulsion base is prepared by adding to a vessel the deionized water and commencing agitation with heating to 80°C. Then the tetrasodium EDTA is added followed by the sodium benzoate and these are dissolved. This is followed by addition of ceteareth. The homogenizer is then turned on and the cetyl alcohol and stearyl alcohol are added keeping the temperature above 80°C. When homogenized, the mixture is cooled to 60°C when phenoxytol is added. At 40°C the homogenizer and mixer is stopped and the mixture is left to thicken for 60 minutes.

The final dye base is made by adding the emulsion base to a vessel, followed by addition of the dye premix solution, and the resulting mixture is mixed until homogeneous. Ammonium hydroxide is added followed by mixing and addition of the pH premix. Water is added to 100% and mixed until homogeneous.

In the examples above, water is used as the diluent. However in variations hereof water can be replaced, in part, by from about 0.5% to about 50% by weight of the total water content of the examples by diluents such as lower alcohols, e.g., ethylene glycol, ethylene glycol monoethyl ether, diethylene glycol, diethylene glycol monoethyl ether, propylene glycol, 1,3-propanediol, ethanol, isopropyl alcohol, glycerine, butoxyethanol, ethoxydiglycol, hexylene glycol, polyglyceryl-2-oleyl ether and mixtures thereof.

Any of Examples I-XV above is mixed in a 1:1 ratio with the conditioning composition below in Example XVI or Example XVII.

Example XVI is commercially available Pantene Pro-V Vitalising Conditioner - Balanced for normal hair, to which a solution of hydrogen peroxide has been added such that Example XVI contains 6% by weight of hydrogen peroxide. Example XVII is commercially available Pantene Pro-V Vitalising Conditioner- Moisturising for Dry or Damaged Hair, to which a solution of hydrogen peroxide has been added such that Example XVII contains 6% by weight of hydrogen peroxide.

The hair colouring and conditioning compositions obtained by mixing any of Examples I-XV with either Example XVI or Example XVII in a 1:1 ratio, provide a complete range of colours, i.e. from blondes to blacks, while providing superior hair conditioning. The compositions are applied to wet hair about 4 times a week after shampooing and left on the hair for about 1-5 minutes before being rinsed off. This method of conditioning the hair using short multiple

applications (eg. 1.5 mins x 14 cycles) instead of a single application lasting about 20 minutes, provides a greater colour change without being any more damaging to the hair.

Hence according to another aspect of the present invention there is provided a method of altering the colour of the hair comprising applying to the hair a hair colour altering composition, such that when the composition is used in the Multiple Application Delta E Technical Test Method as described hereinbelow the composition gives a value of Delta E which is the same as or more than the value of Delta E when the composition is applied to the hair in a single application and left on the hair for 20 minutes before being rinsed as described in the Single Application Delta E Technical Test Method as described hereinbelow.

It is preferred that the hair colouring compositions of the invention provide a Delta E value of greater than about 8, preferably greater than about 10, more preferably greater than about 12, most preferably greater than about 15, and especially greater than about 20, as measured by the test method below.

Delta E Technical Test Method

I Assessment of Initial Color and Color Change

Assessment of color change

The equipment used to measure both the initial color and color change on substrates (hair / skin) dyed with the colouring and conditioning compositions of the present invention is a Hunter LabScan spectrophotometer. The value used to express the degree of color change on any particular substrate is Delta E (ΔE). Delta E, as defined herein, is represented by a factual sum of L, a, and b values such that:

$$\Delta E = (\Delta L^2 + \Delta a^2 + \Delta b^2)^{1/2}$$

and L, a, b represent values from the CIELab colour space as defined by Commission Internationale de L'Eclairage (CIE). According to this definition, L is a measure of lightness and darkness, wherein L = 100 is equivalent to white, and L = 0 is equivalent to black. Further, 'a' is a measure of the red and green quotients (color hues) such that positive equates to red and

negative equates to green, and 'b' is a measure of the yellow and blue quotients (color hues) such that positive equates to yellow and negative equates to blue.

Hunter LabScan Colorimeter is a full scanning spectrophotometer with a wavelength of from 400-700 nanometers which records the color of test hair switches (tresses) in terms of 'L', 'a' and 'b' values. The machine is set to: mode - 0/45; port size - 1/2 inch; view size - 1/2 inch; light - D65; field of view - 10°; UV lamp/filter - none. The hair is placed in a sample holder designed to hold the hair in a uniform orientation during measurement. Equivalent colorimeters can be used, but it must be ensured that the hair does not move during measurement. The hair must be spread to cover the port during color measurement. Dots are placed on the switch holder to guide the positioning of the holder at the port. The dots are lined up with a mark on the port and readings are taken at each spot.

Eight measurements are run per switch, 4 on each side.

Standard hair switch

The compositions according to the present invention can be used to color hair of all colors, types and condition. For the purposes of illustration, grey hair switches are used. These standard hair switches can be measured in terms of their approximate L, a, b values.

	L	a	b
Grey hair switch	75	4	27

Hair switch colouring method - Single Application Delta E Test Method

To color hair, a 4 gram switch of about 8 inch long hair is hung over a suitable container and wetted for 30 seconds. The test colouring product is then prepared (i.e., where applicable the separate bottle components are mixed together) and about 5.6 grams of product is applied directly to the test hair switch. The colorant is massaged through the hair switch for up to about 1 minute and then left on the hair switch for about 20 minutes. After rinsing with running water

for about 2 minutes the colored hair switch is dried using a hair drier. The color development of the colored and dried test hair switch can then be assessed using the Hunter LabScan spectrophotometer.

Hair switch colouring method - Multiple Application Delta E Test Method

To colour hair, a 4 gram switch of about 8 inch long hair is hung over a suitable container and wetted for 30 seconds. The test colouring product is then prepared (i.e., where applicable the separate bottle components are mixed together) and about 0.4 grams of product is applied directly to the test hair switch. The colorant is massaged through the hair switch for up to about 30 seconds and then left on the hair switch for about 1 minute. After rinsing with running water for about 2 minutes the colored hair switch is dried using a hair drier. The color development of the colored and dried test hair switch can then be assessed using the Hunter LabScan spectrophotometer. The above protocol is repeated for further 13 cycles. The final colour development of the dried test hair switch is assessed using the Hunter LabScan spectrophotometer and represents 14 applications of the colouring and conditioning composition.

Results

The test method above was carried out on Example A to compare delta E values obtained when using both the multi-application method and the single application method. Example A was a hair colouring and conditioning composition prepared by mixing the composition in Example XII above with commercially available Pantene Pro-V Vitalising Conditioner-Balanced for Normal Hair to which a solution of Hydrogen Peroxide has been added, such that the level of hydrogen peroxide in the conditioner composition is 6% by weight of the conditioner composition. Example XII and the hydrogen peroxide containing conditioner composition were mixed in a 1:1 ratio.

Cycles	Delta E
0	0
2	9.52
3	13.66
4	16.45

5	19.08	
6	20.64	
7	22.83	
8	24.79	
9	25.94	
10	26.89	
11	27.69	
12	29.03	
13	31.14	
14	31.37	22.03*

*= Single application of 21 minutes

As can be seen from the above table, when Example A is applied to the hair according to the multi-application method a bigger colour change is obtained compared with a single application of 21 minutes.

In addition, the results from the Combing Test Method below show that a similar amount of damage is inflicted on the hair using multiple application method of the present invention compared with using a "one-shot" single treatment method lasting about 20-30 minutes.

Combing Technical Test Method

As mentioned above, the multiple application method of the present invention provides a bigger colour change compared to a conventional single application method. It has also been found that the method of the present invention provides improved ease of combing of the hair compared with a single use application. It is preferred that the hair colour altering compositions used in the present methods provide an Average Combing Index Value of 1.2 or greater, preferably of 1.5 or greater, more preferably 1.8 or greater, most preferably 2.0 or greater as measured by the Combing Technical Test Method described below.

It is also preferable that the hair colouring and conditioning compositions of the present invention provide a Combing Index Value after 1 cycle of greater than 1.1 and a Combing Index Value after 6 cycles of greater than 1.1.

The hair switches used in this test method are medium brown virgin hair, weighing 6 grams and being 10 inches in length. Five of these hair switches are treated with the hair colouring and conditioning compositions of the present invention as follows.

Treatment of switches with colouring and conditioning compositions

Colouring and conditioning compositions to be tested are prepared just before the product application, (for example, by mixing a first component containing oxidative hair colouring agents with a second component containing hydrogen peroxide). The switch is hung above a sink and wetted for 30 seconds with water at 100°F and 1.5 gpm pressure and 8-15 grains water hardness where in the test method 1 grain is equivalent to 17.1ppm of calcium and/or magnesium ions. (The same water hardness is used throughout the experiment). Excess water is squeezed out of the switch. 1.2grams of the colouring composition to be tested is applied on the top end of the switch and spread evenly down to the bottom end, then milked into the switch for 30 seconds and left on the switch for a further 4.5 minutes (5 minutes total application time). The switch is then rinsed with water at 100°F for 30 seconds. Excess water is squeezed out of the switch.

The above treatment constitutes 1 cycles of application. This cycle is repeated up to 6 times, combing measurements are taken after each cycle. As used herein the term "Combing Index Value" is the Combing Index Value ("CIV") measured after a specified number of cycles. As used herein the term "Average Combing Index Value" is calculated as follows:

$$\text{Average Combing Index Value} = (\text{CIV after 1 cycle} + \text{CIV after 2 cycles} + \text{CIV after 3 cycles} + \text{CIV after 4 cycles} + \text{CIV after 5 cycles} + \text{CIV after 6 cycles}) / 6$$

Combing Measurements

Equipment Needed:

- Instron 5543 tensile tester with IBM compatible computer and Merlin Profiler software
- Instron load cell, 5N maximum capacity with a cross-head adapter
- String with small clip
- Special comb holder for combing measurements
- 295 Hercules Saw Cut 2 Combs, combining "wide teeth" part (4 teeth/cm, 9 cm length) and "narrow teeth" part (10 teeth/cm, 8 cm length)

For each test, 5 hair switches per treatment are used, 5 individual measurements per switch are taken. The switches are treated with the colouring compositions to be tested as described above. The wet switches are measured as soon as the treatment cycle is completed.

The load cell is assembled on the cross-head of the Instron tester. Any load cells are removed from the base of the tester. The string is assembled with the clip on the load cell. The comb holder is secured on the base of the Instron tester with screws. The Instron tester is switched on and the transducer is allowed to equilibrate. The computer is switched on and the Merlin Profiler software is downloaded. [Merlin Profiler software is commercially available from the Instron Corporation]. The conditions outlined in the test profile are as follows:

- Extension speed : 15 mm/sec
- Extension length : 240 mm
- Reading time interval : 0.5 sec

The cross-head of the Instron tester is set into the starting position. This position should ensure the distance from the comb to the top of the hair switch is equal to 20 mm. Each hair switch is taken from the rack and combed 1 time with the big teeth and 1 time with the narrow teeth (combing is repeated if required, until there is no tangle left). The new comb is placed into the holder, such that the narrow teeth part is available for combing. The hair switch is secured in the clip, and the load cell is balanced. The switch is then pressed through the narrow teeth of the comb and secured in position by the deflector. The test method is commenced by activating the moving cross-head.

The test must include one internal control, which is non-treated hair switches wetted with water for 30 seconds (under conditions used with the colouring compositions).

Once all the switches are analysed, the combing work is then calculated for all switches using the following equation (Eq 1.):

$$\text{Work (mJ)} = \int_{x=0}^{x=240} F dx \quad (\text{Eq1})$$

Where: F is the load in the load cell when the switch is pulled over a distance x mm through the comb.

The combing work for each hair switch is averaged. The averages of 5 switches is used to produce an average reading per treatment (Work[treatment]). These readings are then analysed for significant differences between treatments using standard statistical methods.

The actual combing work is converted into index readings, based on the results obtained for the internal control (Eq 2.)

$$\text{Combing Index Value} = \frac{\text{Work[control]}}{\text{Work[treatment]}} \quad (\text{Eq 2.})$$

Results

The test method above was carried out on several hair colouring and conditioning products described below and compared with the same test method where the hair colouring and conditioning products were applied to the hair in a single application and left on the hair for about 30 minutes before being rinsed off. The Combing Index Values obtained were as follows:

Treatment Product	cycle 1	cycle 2	cycle 3	cycle 4	cycle 5	cycle 6	30 min*
Example A ¹	1.6	1.7	2.0	2.2	2.1	2.1	2
Example B ²	1.6	1.7	1.8	2.1	2.0	1.9	1.6

* 30 min single application

1. Example A is a hair colouring and conditioning composition prepared by mixing the composition Example XII below with commercially available Pantene Pro-V Vitalising Conditioner- Balanced for Normal Hair to which a solution of Hydrogen Peroxide has been added, such that the level of hydrogen peroxide in the conditioner composition is 6% by weight of the conditioner composition. Example XII and the hydrogen peroxide containing conditioner composition are mixed in a 1:1 ratio.
2. Example B is a hair colouring and conditioning composition prepared by mixing the composition Example XII below with commercially available Pantene Pro-V Vitalising Conditioner- Moisturising for Dry or Damaged Hair to which a solution of Hydrogen Peroxide has been added, such that the level of hydrogen peroxide in the conditioner composition is 6% by weight of the conditioner composition. Example XII and the hydrogen peroxide containing conditioner composition are mixed in a 1:1 ratio.

The results show that use of a colour altering composition according to a multiple application method gives an equal or greater ease of combing than a 30 minute single application of colour altering composition.

The results of the Combing Method also demonstrate that that there is less hair damage from a multiple application method (eg. 6x5mins) than there is from a "one-shot" single application method (eg. 1 x 30 mins).

Kit Example

An example of a kit according to the present invention is a package having two chambers, one chamber containing the composition of Example XVI or Example XVII and the other chamber containing any one of the compositions of Examples I - XV. The pack has a means of mixing a defined level each of the two compositions within the pack and a means to dispense the resulting hair colouring and conditioning composition. The kit also contains instructions instructing consumers that they should use in the shower on wet hair, after shampooing, in place of their normal conditioning composition, preferably from once and 7 times a week, preferably between about 3 and 5 times a week.

Claims:

1. A method for providing a permanent, semi-permanent or demi-permanent colour change to human or animal hair wherein the method comprises the steps of (a) applying to hair a hair colour altering composition, (b) leaving the hair colour altering composition on the hair for from about 0.5 to about 15 minutes and then (c) optionally rinsing the hair colour altering composition from the hair, wherein steps (a) and (b) and (c) are repeated from about once a month to about 3 times a day.
2. A method according to Claim 1 wherein steps (a), (b) and c are repeated at least 4 times in total, preferably at least 6 times in total.
3. A method according to Claim 1 or 2 wherein the hair colour altering composition comprises less than about 5% by weight of surfactant.
4. A method according to any of Claims 1 to 3 wherein the hair colour altering composition comprises less than about 5% by weight of anionic surfactant.
5. A method according to any of Claims 1 to 4 wherein the hair colour altering composition has a pH of from about 2 to about 13, preferably from about 9 to about 11
6. A method according to any of Claims 1 to 5 wherein the hair colour altering composition is left on the hair for from about 0.5 to about 5 minutes.
7. A method according to Claim 1 or 6 wherein the hair colour altering composition is left on the hair for from about 1 minute to about 5 minutes, preferably from about 1 minute to about 3 minutes.
8. A method according to Claims 1 to 7 wherein steps (a), (b) and (c) are repeated from about once a week to about 7 times a week, preferably from about 2 times a week to about 6 times a week, preferably from about 2 to about 4 times a week.

9. A method according to Claims 1 to 8 wherein steps (a), (b) and (c) are repeated from 2 times to about 6 times per week, preferably from about 2 times to about 4 times per week.
 10. A method according to any of Claims 1 to 9 wherein the hair colour altering composition is applied to wet hair.
 11. A method according to any of Claims 1 to 10 wherein the hair colour altering composition is rinsed from the hair after step (b).
 12. A method according to any of Claims 1 to 11 wherein the hair colour altering composition provides a permanent colour change to the hair.
 13. A method according to Claims 1 to 12 wherein the hair colour altering composition comprises an oxidative hair colouring agent.
 14. A method according to Claims 1 to 13 wherein the hair colour altering composition comprises a hair conditioning agent.
 15. A method according to Claims 1 to 14 wherein the hair colour altering composition comprises an oxidising agent.
 16. A method according to any of Claims 1 to 15 wherein the method additionally comprises the step of shampooing the hair immediately before step (a).
 17. A method according to any of Claims 1 to 16 wherein the method can be used in the shower.
-
18. A hair colour altering kit comprising (a) a hair colour altering composition and (b) a set of instructions for using said hair colour altering composition according to the method of any of Claims 1 to 17.
 19. A method of altering the colour of the hair comprising applying to the hair a hair colour altering composition, such that when the composition is used in the Multiple Application

Delta E Technical Test Method as described hereinabove the composition gives a value of Delta E which is the same as or more than the value of delta E when the composition is applied to the hair in a single application as described in the Single Application Delta E Technical Test Method as described hereinabove.

20. A method according to Claim 19 wherein the composition gives an Average Combing Index Value of greater than 1.1, preferably greater than 1.5, more preferably about 2.0, when the composition is used in the Combing Technical Test Method described hereinabove.

21. A method according to Claim 19 or 20 wherein the composition gives a Combing Index Value after 1 cycle of greater than 1.1 and a Combing Index Value after 6 cycles of greater than 1.1 as measured by the Combing Technical Test Method described hereinabove.

22. A method according to Claim 19 wherein the composition provides a Combing Index Value after 6 cycles as measured by the Combing Value Technical Test Method which is the same as or more than the Combing Index Value given when the composition is applied to the hair in a single application and left on the hair for 30 minutes.

23. A kit according to claim 18 additionally comprising an initial colouring composition suitable for providing an initial colour to hair, wherein the colour provided by the hair colour altering composition (a) is substantially the same shade as the initial colouring composition.

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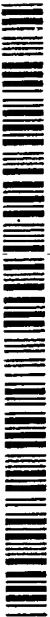
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WO 01/76546 A3

(54) Title: METHOD FOR COLOURING HAIR

(57) Abstract: A method of providing a colour change to human or animal hair wherein the method comprises the steps of (a) applying to hair a hair colour altering composition, (b) leaving the hair colour altering composition on the hair for from about 0.5 to about 15 minutes and then (c) optionally, rinsing the hair colour altering composition from the hair, wherein steps (a) and (b) and (c) are repeated from about once a month to about 3 times a day. A multiple application method of the invention provides an increase in colour change (as measured by Delta E) compared with conventional methods which use a single application of hair colouring composition for around 20-30 minutes. In addition, the method of the present invention is no more damaging to the hair compared with conventional single application methods.

INTERNATIONAL SEARCH REPORT

Intern. Application No

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A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 A61K7/13 A61K7/135

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 A61K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 104 021 A (H. LAPIDUS ET AL.) 1 August 1978 (1978-08-01) column 3, line 41 - line 68; claims 1-16; example 1 ---	1-7, 11-13, 15,17
X	WO 98 52520 A (PROCTER & GAMBLE) 26 November 1998 (1998-11-26) claims 1-26; example 1 ---	1-7, 11-13, 15,17,18
X	GB 2 259 717 A (KAO) 24 March 1993 (1993-03-24) page 8, line 10 -page 9, line 24; claims 1-10; example 5 ---	1-9,11, 14,17

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Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 190 064 A (H.W. GORDON ET AL.) 26 February 1980 (1980-02-26) column 7, line 20 - line 44; claims 1-4,8 -----	1,3,5-7, 14,17

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box I.2

Claims Nos.: 19-22

Present claims 19-22 relate to a method defined (inter alia) by reference to the following parameter(s):

P1: "Multiple Application Delta E Technical Test Method" and "Single application Delta E Technical Test Method" (claim 19)

P2: "Average Combing Index Value" and "Combing Technical Test Method" (claims 20-22)

The use of these parameters in the present context is considered to lead to a lack of clarity within the meaning of Article 6 PCT. It is impossible to compare the parameters the applicant has chosen to employ with what is set out in the prior art. The lack of clarity is such as to render a meaningful complete search impossible. Consequently, the search has been restricted to : 1-18 and 23.

The applicant's attention is drawn to the fact that claims, or parts of claims, relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure.

INTERNATIONAL SEARCH REPORT

Information on patent family members

Intern. Application No

PCT/US 01/10490

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 4104021 A	01-08-1978	AT 372276 B	26-09-1983
		AT 372177 A	15-02-1983
		AU 507404 B2	14-02-1980
		AU 2557877 A	30-11-1978
		BE 855170 A1	16-09-1977
		BR 7703373 A	28-02-1978
		BR 7703464 A	14-03-1978
		CA 1073817 A1	18-03-1980
		CH 623741 A5	30-06-1981
		DE 2722979 A1	08-12-1977
		DK 235077 A	29-11-1977
		FI 771683 A ,B,	29-11-1977
		FR 2352542 A1	23-12-1977
		GB 1542034 A	14-03-1979
		GR 82248 A1	13-12-1984
		IE 45066 B1	16-06-1982
		JP 52148634 A	10-12-1977
		JP 59231009 A	25-12-1984
		LU 77379 A1	29-08-1977
		MX 148039 A	08-03-1983
		NL 7705458 A ,B,	30-11-1977
		NO 771707 A ,B,	29-11-1977
		PH 13324 A	13-03-1980
		PT 66609 A ,B	01-06-1977
		SE 7705460 A	29-11-1977
		ZA 7702755 A	26-04-1978
WO 9852520 A	26-11-1998	AU 7590398 A	11-12-1998
		AU 7590998 A	11-12-1998
		AU 7591098 A	11-12-1998
		AU 7591398 A	11-12-1998
		AU 7692198 A	11-12-1998
		BR 9809462 A	20-06-2000
		BR 9809463 A	20-06-2000
		BR 9809464 A	20-06-2000
		BR 9811702 A	25-07-2000
		BR 9811703 A	25-07-2000
		CN 1261777 T	02-08-2000
		CN 1261778 T	02-08-2000
		CN 1263457 T	16-08-2000
		CN 1264285 T	23-08-2000
		CN 1264286 T	23-08-2000
		EP 1011618 A1	28-06-2000
		EP 1006989 A1	14-06-2000
		EP 1006990 A1	14-06-2000
		EP 1003466 A1	31-05-2000
		EP 0989841 A1	05-04-2000
		HU 0001230 A2	28-09-2000
		JP 2001504860 T	10-04-2001
		JP 2001504861 T	10-04-2001
		JP 2001504862 T	10-04-2001
		JP 2001504863 T	10-04-2001
		JP 2001507374 T	05-06-2001
		WO 9852519 A1	26-11-1998
		WO 9852520 A1	26-11-1998
		WO 9852521 A1	26-11-1998
		WO 9852522 A1	26-11-1998
		WO 9852523 A1	26-11-1998

INTERNATIONAL SEARCH REPORT

Information on patent family members

Intern. Application No

PCT/US 01/10490

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9852520	A	HU 0002773 A2	28-12-2000
		ZA 9804328 A	30-11-1998
		HU 0002695 A2	28-12-2000
		ZA 9804327 A	30-11-1998
GB 2259717	A 24-03-1993	JP 2017387 C	19-02-1996
		JP 5078228 A	30-03-1993
		JP 7037370 B	26-04-1995
US 4190064	A 26-02-1980	NONE	